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Palladium catalyzed multicomponent reactions in ordered sequence: new syntheses of *o*,*o*′-dialkylsubstituted diarylacetylenes and diarylalkylidenehexahydromethanofluorenes

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Abstract

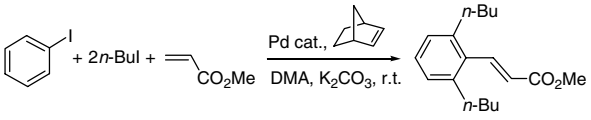
Catalytic one-pot reactions of aromatic iodides with alkyl halides, phenylacetylene or diphenylacetylene, potassium acetate or carbonate, norbornene and palladium acetate in DMF or DMA are reported. A high selectivity towards dialkylsubstituted diarylacetylenes and diarylalkylidenehexahydromethanofluorenes, respectively, has been reached.

Keywords: Palladium; Palladacycles; Catalysis; Multicomponent reactions; C–H Activation; Aromatic functionalization

1. Introduction

The invention of new palladium reagents and catalysts has extensively affected the way to carry out organic syntheses [1]. Some years ago, we described a palladacycle-based catalytic methodology which allowed the achievement of highly selective sequential reactions in one pot starting from a molecular pool [2].

Thus for example from iodobenzene, *n*-butyl iodide, methyl acrylate and potassium carbonate in the presence of norbornene and palladium acetate in dimethylacetamide (DMA) at 20 °C we obtained methyl *o*,*o*′-di-*n*-butylcinnamate in 93% yield.



(1)

The reaction occurred according to Scheme 1 (X = I (Br); Y = I, Br, Cl; R = alkyl; L = solvent or coordinating molecule), which was proved by the isolation and characterization of products and intermediates, both organic and organometallic [2,3].

Oxidative addition by aryl halide to palladium(0) gives the arylpalladium complex **1** [4]. Norbornene insertion into the arylpalladium bond occurs stereoselectively and leads to the *cis*,*exo* arylnorbornylpalladium species **2** [5] which readily undergoes cyclisation to the five membered palladacycle **3** [6]. The alkyl halide oxidatively adds to complex **3** to form the palladium(IV) species **4** [3,7] which spontaneously converts into the norbornylpalladium(II) complex **5** [3,8]. This reductive elimination occurs through selective migration of the alkyl group to the aromatic site of palladacycle **4**. Once complex **5** is formed, conditions become favourable for repeating ring closure to afford complex **6**. A new oxidative addition and reductive elimination sequence leads to the arylnorbornylpalladium species **8**, containing the *o*,*o*′-dialkylated aryl moiety. At this point

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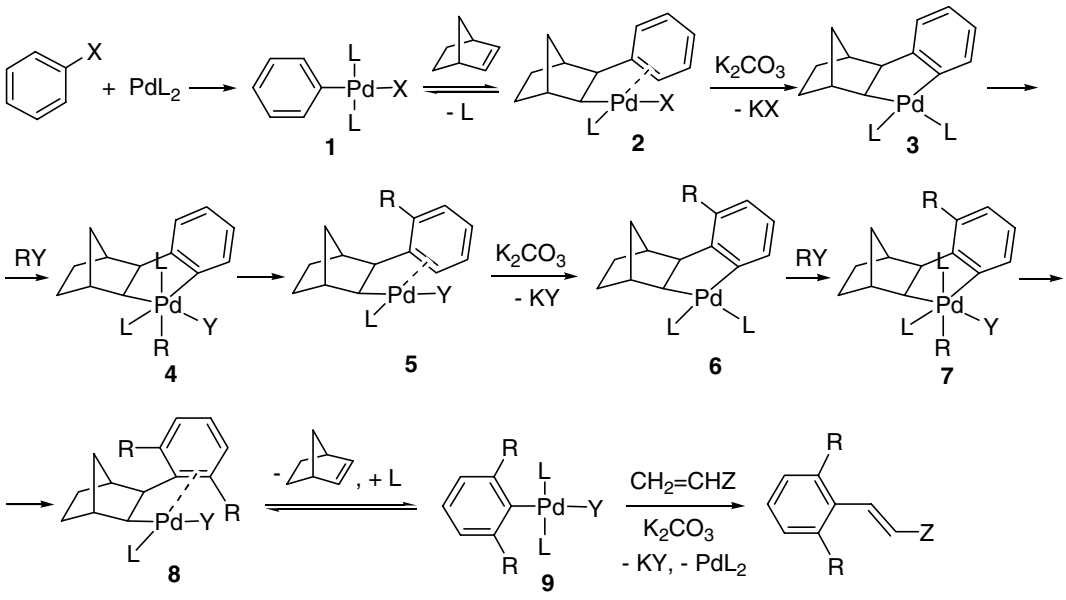


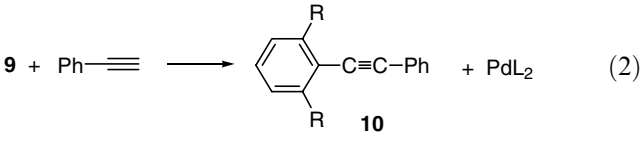
Scheme 1.

norbornene deinsertion [3a,9] occurs spontaneously with formation of the dialkylated arylpalladium complex **9**, which reacts with the terminal olefin [2,10].

As shown in Scheme 1 the final step, corresponding to a Heck-type reaction [11], plays a key role in providing both the organic product and palladium(0), the latter acting as a catalyst.

This step could be replaced by other reactions such as the Suzuki one [12] able to lead to liberation of palladium(0).

Along this line of reasoning we wondered whether the final stage could be achieved taking advantage of the Cassar–Sonogashira reaction as shown below [13].



(2)

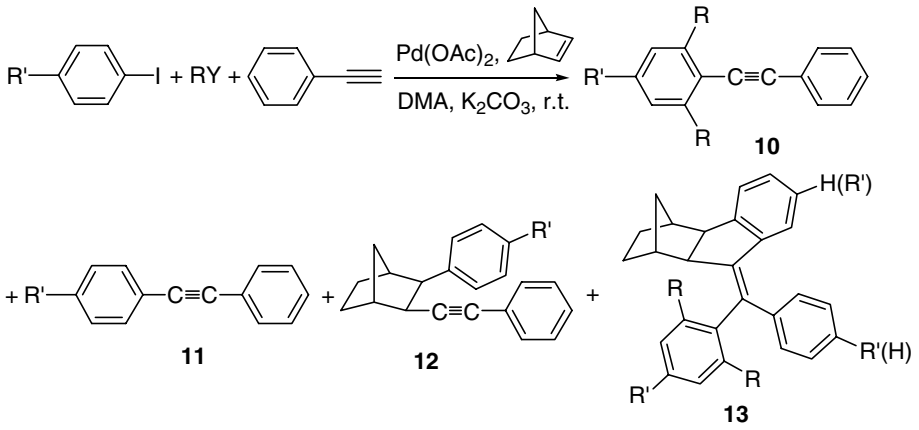
Our investigation led to unexpected results which are reported here.

2. Results and discussion

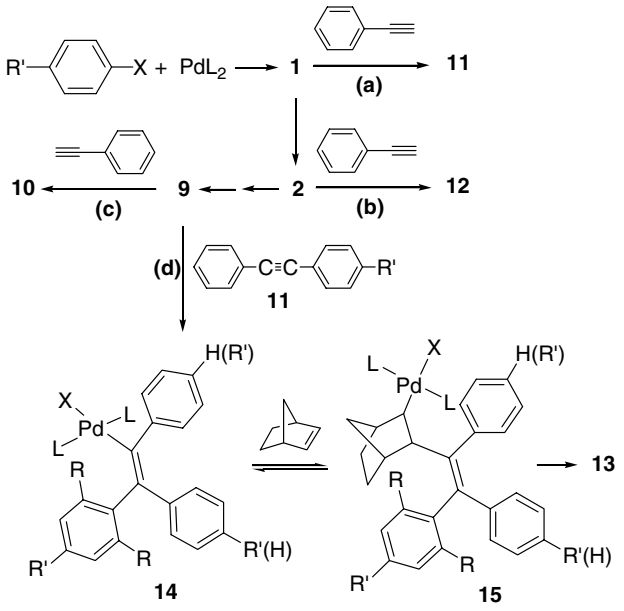
The reaction of an aryl iodide, an alkyl bromide, norbornene, phenylacetylene and potassium carbonate in the presence of palladium acetate in DMA as solvent at room temperature led to a complex mixture of products. Keeping the conversion low (30%) the mixture could be simplified to the compounds **10**, **11**, **12** and **13** (Scheme 2; R = *n*-Pr; R′ = H) which were isolated in 8%, 2%, 2% and 12%, respectively, starting from iodobenzene and *n*-propyl bromide.

A careful optimisation work led us to establish conditions for obtaining compound **10** with good selectivity. This implied first understanding the reaction course. Scheme 3 depicts the various competitive reactions involved.

As shown in Scheme 3, phenylacetylene reacts at different stages of the sequential process: in (a) it gives the known Cassar–Sonogashira reaction [13] leading to the diphenylacetylene derivative **11**; in (b) it interacts with the arylnorbornylpalladium halide complex **2** [5], resulting from norbornene insertion into the arylpalladium halide originally formed, according to a pathway previously reported [14]; in (c) it interacts with the final complex **9** to give the desired product **10**; in (d) diphenylacetylene **11** formed by reaction of phenylacetylene with the arylpalladium(II) complex **1** (way (a)), reacts with palladium complex **9** to form the vinylpalladium species **14** (two regioisomers, depending on the direction of addition of the Ar–Pd–X species to the triple bond, when R′≠H). This time norbornene can be inserted and the resulting complex **15** can readily close a cyclopentene ring giving rise to **13**. The role played by norbornene in the reaction leading to the formation of compound **13** is worth noting. It inserts into the initial arylpalladium complex **1** to give **2**. Then, through formation of two consecutive palladacycles it allows the selective activation towards alkylation of the *ortho* aromatic C–H bonds (from **3** to **8**). After introduction of the two alkyl groups in the aromatic ring (complex **8**) it deinserts to give **9** and, replaced by the diphenylacetylene derivative, it immediately reinserts when the steric constrain is removed.



Scheme 2.



Scheme 3.

Based on the knowledge reported above we devised two ways for obtaining either **10** or **13** selectively.

2.1. Synthesis of compounds *10*

To obtain **10** we had to modify the original conditions in which the aryl iodide, the alkyl bromide, phenylacetylene, norbornene, potassium carbonate and palladium acetate were used in 10:30:10:10:30:1 molar ratio, according to the following criteria:

(1) in order to favor norbornene insertion leading to **2** rather than reaction (a) of Scheme 3, the use of potassium acetate in place of potassium carbonate proved to be effective. The role of the acetato anion in favoring the insertion process is reported [9,15], moreover it better controls the reactivity of phenylacetylene, in so far as in comparison with potassium carbonate it leads to lower amounts of both **11** and **12**;
(2) a large excess of alkyl bromide, which was gradually added to the reaction mixture, helped to accelerate the reactions leading from **2** to **9** in respect to way (b);
(3) DMA was slightly better than DMF as solvent;
(4) the temperature had a favourable effect on the rate but increased the amount of by-products, so it was kept at 25 °C;
(5) the gradual addition of phenylacetylene prevented undesired reactions of the latter.

With a molar ratio of 10:(20–40, gradual addition):(4–12, gradual addition):12:60:1 (referred to the reagents shown above with potassium acetate in place of potassium carbonate), we obtained a 71% yield of compound **10b** (Table 1. R = *n*-Pr; R′ = H) for an 84% conversion of iodobenzene. The yields of **11**, **12** and **13** (R′ = H) then were curtailed to 4%, 3% and 2%, respectively. The reaction was carried out at 25 °C for 144 h. The presence of electron-withdrawing substituents in *para* to the aryl iodide slightly increased the yield while varying R in the alkyl bromide resulted in the ethyl group giving the best yield (Table 1).

Experiments with other monosubstituted alkynes showed that under the same conditions alkylacetylenes converted to a small extent (18% with butylacetylene), while both electronwithdrawing and electronreleasing substituents in the *para* position of phenylacetylene decreased conversion.

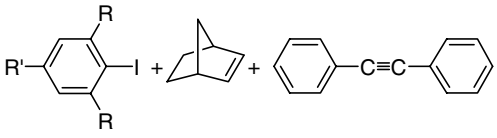
2.2. Synthesis of compounds *13*

To obtain compounds **13** selectively we started from an *ortho*,*ortho*′-disubstituted aryl iodide, diphenylacetylene and norbornene, potassium carbonate and palladium acetate in the ratio 10:12:12:20:1 at 105 °C in DMF.

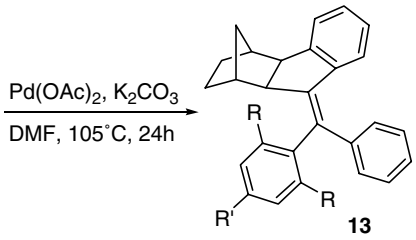
Table 1
Reaction of an aryl iodide and an alkyl bromide with phenylacetylene in the presence of $Pd(OAc)_2$ and norbornene as catalysts and KOAc as a base[a]

Run	R′	R	Yield[b] (%)				Selectivity[c] (%) of **10**
1	H	Et	**10a** 77	–	–	–	90
2	H	*n*-Pr	**10b** 71	**11** 4	**12b** 3	**13** 2	84
3	H	*n*-Bu	**10c** 66	**11** 7	**12b** 5	–	82
4	4-Me	*n*-Pr	**10d** 68	**11** 5	–	–	83
5	4-F	*n*-Pr	**10e** 79	**11** 1	–	**13**[d]2	89

[a] Initial molar ratio of the reagents in the order reported in the title (in brackets after addition of alkyl bromide and terminal acetylenic compound by syringe pump): 10:20 (40):4 (12):1:12:60; 25 °C, 144 h, DMA as solvent, under nitrogen.
[b] Compounds **10**: isolated yield based on the charged amount of the aryl iodide; compounds **11**, **12** and **13**: GC yield.
[c] Based on converted aryl iodide.
[d] Two regioisomers are formed (Scheme 3).



R = alkyl; R' = H, alkyl



(3)

Eq. (3) represents the reaction, Table 2 reports significant results. It is worth noting that reaction (3) proceeded at 105 °C without significant formation of by-products and that potassium acetate was not needed to accelerate norbornene insertion. On the other side, K_2CO_3 is more effective than KOAc in promoting the final ring closure to compound **13**.

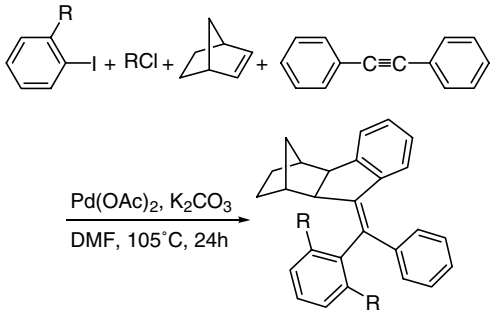
The aryl iodide to palladium acetate molar ratio was not optimised. That the use of higher ratio is possible was shown by carrying out run 1 with a 100:1 molar ratio with the same yield. Among the olefins tested only norbornene and bicyclooctene gave excellent results. Norbornadiene gave a complex mixture while benzo-7-oxanorbornene and 5,6-dimethoxycarbonyl-7-oxanorbornene did not lead to the desired products. The good performance of bicyclooctene is noteworthy because it shows that the primary requirement for palladacycle formation is not the presence of a strained double bond but the reluctance to β-hydrogen elimination.

Table 2
Reaction of an *o*,*o*′-disubstituted aryl iodide, diphenylacetylene and a rigid olefin in the presence of $Pd(OAc)_2$ as catalyst and K_2CO_3 as a base[a]

Run	R, R′	Olefin	Yield[b] (%)
1	Me, H	Norbornene	**13a** 87
2	Et, H	Norbornene	**13b** 90
3	*i*-Pr, H	Norbornene	**13c** 92
4	Me, Me	Norbornene	**13d** 91
5	Me, Me	Bicyclooctene	**16** 89

[a] Molar ratio of the reagents in the order reported in the title: 10:12:12:1:20; 105 °C, 24 h, DMF as solvent, under dinitrogen.
[b] Isolated yield based on the charged amount of the aryl iodide.

An alternative way to **13** starts from a mono-*o*-substituted aryl iodide according to the following reaction:



13e (R = *n*-Pr, 70%)
13f (R = *n*-Bu, 94%)

(4)

Alkyl chlorides are used in this case in place of the bromides which are too unstable at 105 °C. The reaction of *o*-substituted aryl iodides requires the introduction of a second R group through norbornene insertion, palladacycle formation and *ortho*-alkylation before norbornene expulsion to afford **9** as shown in Scheme 1 (from **5** to **8**). Unsubstituted aryl iodides cannot be used because other patways prevail.

It has to be observed that the reaction of the iodoarene with diphenylacetylene leading to a phenanthrene derivative reported by Dyker and Kellner [16] does not occur, presumably because of the competitive norbornene insertion at the level of complex **14**. The present reaction is indeed completely stereoselective, only *cis* addition of the arylpalladium halide to the triple bond taking place without any isomerisation of the resulting vinylpalladium complex (Scheme 3).

The way to compounds **13** offers an easy access to a class of tetrasubstituted olefins. The literature reports examples based on insertion of diarylacetylenes into aryl palladium iodide complexes followed by a Suzuki-type

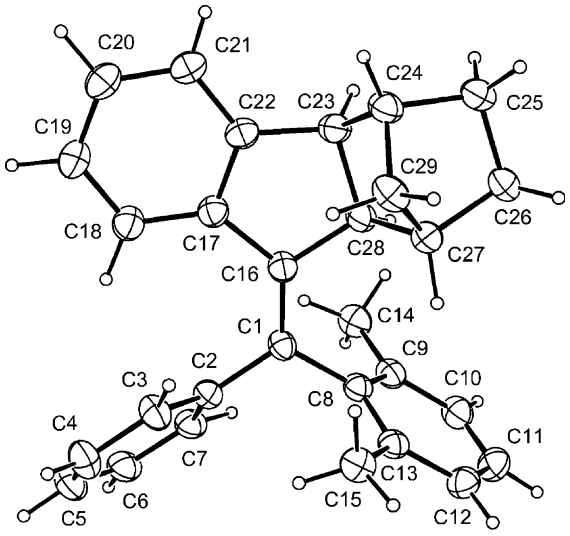


Fig. 1. ORTEP [19] projection of compound **13a** (R = Me; R′ = H) with arbitrary numbering scheme. The ellipsoids are at 30% probability level.

reaction [17] or on intramolecular triple bond insertion, followed by norbornene insertion and cyclisation [18].

To confirm the structure of the hexahydromethanofluorene the crystal structure **13a** (R = Me; R′ = H) was solved and is reported in Fig. 1. The single aromatic rings are planar within the errors. The two single phenyl rings C2–C7 and C8–C13 are oriented in such a way that their mean planes form a dihedral angle of 75.7(3)° to each other. The two six- (C17–C22) and five-membered (C16, C17, C22, C23, C28) mean ring planes form a dihedral angle of 3.1(3)°, while their mean plane form dihedral angles of 63.1(3)° and 101.8(3)° with those of the two above quoted phenyl rings, respectively. In the solid state the molecules are connected through normal van der Waals contacts.

3. Conclusion

In conclusion, the alkyne reaction studied was found to be much more complex than expected. In spite of this it has been possible to obtain the synthesis of selectively substituted diarylalkynes and diarylalkylidenehexahydromethanofluorenes in good to excellent yields.

4. Experimental

4.1. General

Most starting materials were commercial products and used as received. 2-Ethyliodobenzene, 2-*n*-propyliodobenzene, 2-*n*-butyliodobenzene, 2,6-dimethyliodobenzene, 2,6-diethyliodobenzene, 2,6-disopropyliodobenzene and 2,4,6-trimethyliodobenzene were prepared by iodination of the corresponding diazonium salt according to the literature [20]. Known compounds (**11**: R′ = Me [21], R′ = F [22], **12**: R′ = H [14a]) were identified by comparison with the literature data. DMA and DMF were dried and stored over 4 Å molecular sieves under nitrogen. Reactions were carried out using Schlenk-line techniques under an atmosphere of nitrogen. A syringe pump from Sage Instruments (Orion Research) was used. Thin layer chromatography was carried out on silica plates (Merck $60F_{254}$) and detection was made by irradiation at 254 nm. Products were isolated by flash column chromatography on silica gel (ICN silica gel 63-200, 60 Å) using hexane as eluent. GC analyses were carried out with a Carlo Erba HRGC 5300 instrument equipped with a 30 m SE-30 gas capillary column and a Hewlett–Packard 3394 integrator. Unless indicated otherwise, ^{1}H and ^{31}C NMR spectra were recorded in $CDCl_3$ at 20 °C using the solvent as internal standard (7.26 and 77.00 ppm for ^{1}H and ^{31}C) on a Bruker AC300 spectrometer operating at 300.1 and 75.4 MHz, respectively. Assignments are based on decoupling and two-dimensional experiments. One or more asterisks indicate interchangeable assignments. EI and CI mass spectra (*m*/*z*, relative intensity (%)) were registered with a Finnigan Mat SSQ 710 instrument. Melting points were measured with an Electrothermal instrument and are uncorrected.

4.2. General procedure for the synthesis of compounds *10*

4.2.1. Reaction of aryl iodides, alkyl bromides and phenylacetylene

A DMA solution (4 ml) containing the aryl iodide (0.60 mmol), the alkyl bromide (1.20 mmol), the acetylenic derivative (0.24 mmol) and norbornene (0.60 mmol) was introduced under nitrogen into a Schlenk-type flask containing $Pd(OAc)_2$ (0.06 mmol) and KOAc (3.60 mmol). To the resulting mixture a solution of the alkyl bromide (1.20 mmol) and the acetylenic derivative (0.48 mmol) in DMA (3 ml) was added at r.t. during 72 h by a syringe pump. The reaction was kept under stirring for an addition 72 h. Methanol (0.5 ml) was then added and the mixture was kept under an atmosphere of CO to allow complete precipitation of palladium black. The resulting mixture was diluted with dichloromethane (ca. 15 ml), was filtered through a celite pad and was extracted with water (3×10 ml). The organic layer was dried over Na_2SO_4; the solvent was rotary-evaporated and the products were isolated by flash column chromatography using hexane as eluent.

4.2.2. 2,6-Diethyl-1,1′-(1,2-ethynediyl)bisbenzene (*10a*: *R* = *Et*; *R′* = *H*)

Yield: 77%; iodobenzene conversion 85%. ^{1}H NMR: δ 7.59–7.53 (2H, m, H2′, H6′), 7.43–7.32 (3H, m, H3′,

H5′, H4′), 7.23, 7.12 (3H, AB_2 system, J = 7.6 Hz, H4, H3, H5), 2.35 (4H, quart., J = 7.5 Hz, 2CH_2Ar), 0.75 (6H, t, J = 7.5 Hz, 2CH_3); ^{13}C NMR: δ 146.5 (q), 131.3 (C2′, C6′), 128.4 (C3′, C5′), 128.2 (C4), 128.0 (C4′), 125.3 (C3, C5), 123.9 (q), 121.5 (q), 96.8 (C≡), 86.6 (C≡), 28.1 (2CH_2Ar), 14.8 (2CH_3); MS: M^+ 234 (80), *m/z* 219 (40), 205 (100), 204 (47), 203 (40), 202 (37), 115 (21), 91 (22).

4.2.3. 2,6-Di-n-propyl-1,1′-(1,2-ethynediyl)bisbenzene (**10b**: R = n-Pr; R′ = H)

Yield: 71%; iodobenzene conversion 84%. ^{1}H NMR: δ 7.55–7.49 (2H, m, H2′, H6′), 7.41–7.30 (3H, m, H3′, H5′, H4′), 7.17, 7.07 (3H, AB_2 system, J = 7.6 Hz, H4, H3, H5), 2.85 (4H, m, 2CH_2Ar), 1.74 (4H, m, 2C$H_2$$CH_3$), 1.01 (6H, t, J = 7.3 Hz, 2CH_3); ^{13}C NMR: δ 145.0 (q), 131.3 (C2′, C6′), 128.4 (C3′, C5′), 128.0 (C4′), 127.8 (C4), 126.2 (C3, C5), 124.0 (q), 122.0 (q), 96.6 (C≡), 87.0 (C≡), 37.2 (2CH_2Ar), 23.9 (2*C*$H_2$$CH_3$), 14.2 (2$CH_3$); MS: M^+ 262 (100), *m/z* 247 (17), 233 (65), 219 (48), 205 (72), 204 (52), 203 (55), 202 (70), 191 (43), 189 (32), 155 (32), 129 (27), 115 (32), 91 (65). A 4%, 3% and 2%, respectively, of **11** (R′ = H: diphenylacetylene), **12** (R′ = H [14a]) and **13** (R = *n*-Pr; R′ = H; see below) was detected by GC.

4.2.4. 2,6-Di-n-butyl-1,1′-(1,2-ethynediyl)bisbenzene (**10c**: R = n-Bu; R′ = H)

Yield: 66%; iodobenzene conversion 80%. ^{1}H NMR: δ 7.55–7.49 (2H, m, H2′, H6′), 7.41–7.30 (3H, m, H3′, H5′, H4′), 7.17, 7.07 (3H, AB_2 system, J = 7.6 Hz, H4, H3, H5), 2.87 (4H, m, 2CH_2Ar), 1.70 (4H, m, 2C$H_2$$CH_2$Ar), 1.44 (4H, sext., J = 7.3 Hz, 2C$H_2$$CH_3$), 0.97 (6H, t, J = 7.3 Hz, 2CH_3); ^{13}C NMR: δ 145.3 (q), 131.2 (C2′, C6′), 128.4 (C3′, C5′), 127.9 (C4′), 127.8 (C4), 126.1 (C3, C5), 124.0 (q), 121.9 (q), 96.5 (C≡), 87.0 (C≡), 34.8 (2*C*H_2Ar), 33.0 (2*C*$H_2$$CH_2$Ar), 22.7 (2*C*$H_2$$CH_3$), 14.0 (2$CH_3$); MS: M^+ 290 (60), *m/z* 261 (22), 205 (100), 204 (28), 203 (35), 202 (40), 191 (28), 91 (44). A 7% and 5%, respectively, of **11** (R′ = H: diphenylacetylene) and **12** (R′ = H [14a]) was detected by GC.

4.2.5. 4-Methyl-2,6-di-n-propyl-1,1′-(1,2-ethynediyl)bisbenzene (**10d**: R = n-Pr; R′ = Me)

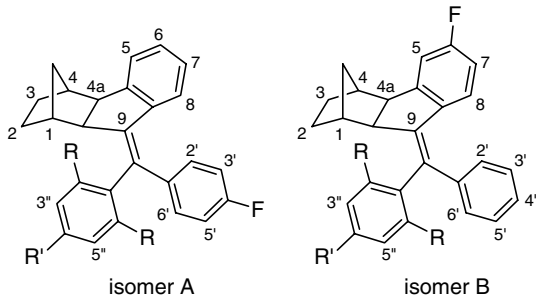
Yield: 68%; 4-iodotoluene conversion 82%. ^{1}H NMR: δ 7.55–7.50 (2H, m, H2′,H6′), 7.41–7.30 (3H, m, H3′, H5′, H4′), 6.91 (2H, br s, H3, H5), 2.83 (4H, m, 2CH_2Ar), 2.34 (3H, s, CH_3), 1.75 (4H, sext., J = 7.4 Hz, 2C$H_2$$CH_3$), 1.03 (6H, t, J = 7.4 Hz, 2CH_3); ^{13}C NMR: δ 144.9 (q), 137.7 (q), 131.2 (C2′, C6′), 128.3 (C3′, C5′), 127.8 (C4′), 127.1 (C3, C5), 124.2 (q), 119.1 (q), 95.9 (C≡), 87.3 (C≡), 37.2 (2*C*H_2Ar), 24.0 (2*C*$H_2$$CH_3$), 21.5 (Ar$CH_3$) 14.2 (2$CH_3$); MS: M^+ 276 (100), *m/z* 261 (12), 247 (35), 233 (30), 219 (48), 218 (32), 215 (30), 205 (24), 204 (24), 203 (30), 202 (46), 115 (30), 105 (30), 91 (70). A 5% of **11** (R′ = Me [20]) was detected by GC.

4.2.6. 4-Fluoro-2,6-di-n-propyl-1,1′-(1,2-ethynediyl)bisbenzene (**10e**: R = n-Pr; R′ = F)

Yield: 79%; 4-fluoroiodobenzene conversion 89%. ^{1}H NMR: δ 7.54–7.48 (2H, m, H2′, H6′), 7.41–7.30 (3H, m, H3′, H5′, H4′), 6.79 (2H, d, $J_{H,F}$ = 9.5 Hz, H3, H5), 2.84 (4H, m, 2CH_2Ar), 1.74 (4H, sext., J = 7.4 Hz, 2C$H_2$$CH_3$), 1.01 (6H, t, J = 7.4 Hz, 2CH_3); ^{13}C NMR: δ 162.14 (d, $J_{H,F}$ = 248.2 Hz, C4), 147.58 (d, $J_{H,F}$ = 7.9 Hz, C2, C6), 131.20 (C2′, C6′), 128.41 (C3′, C5′), 128.04 (C4′), 123.83 (C1′), 118.09 (d, $J_{H,F}$ = 2.9 Hz, C1), 113.15 (d, $J_{H,F}$ = 21.5 Hz, C3, C5), 96.22 (d, $J_{H,F}$ = 1.7 Hz, C≡), 86.15 (C≡), 37.09 (d, $J_{H,F}$ = 1.7 Hz, 2*C*H_2Ar), 23.57 (2*C*$H_2$$CH_3$), 14.03 (2$CH_3$); MS: M^+ 280 (100), *m/z* 251 (31), 237 (20), 223 (45), 222 (29), 221 (30), 220 (35), 209 (27), 161 (20), 91 (33). A 1% and 2%, respectively, of **11** (R′ = F [21]) and **13** (R = *n*-Pr; R′ = F) was detected by GC.

4.2.7. E-9{1-(4″-Fluoro-2″,6″-di-n-propylphenyl)-1-(4′-fluorophenyl)methylene}-1,2,3,4,4a,9a-hexahydro-1,4-methano-1H-fluorene (isomer A) and E-9{1-(4″-fluoro-2″,6″-di-n-propylphenyl)-1-phenylmethylene}-1,2,3,4,4a,9a-hexahydro-1,4-methano-6-fluoro-1H-fluorene (isomer B) (**13**: R = n-Pr; R′ = F); a 1:1 mixture

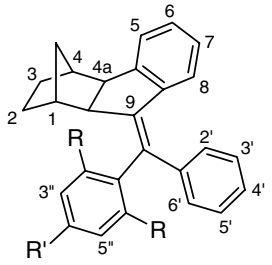
^{1}H NMR (500 MHz): δ 7.37–7.20 (8H, m, H2′, H6′ (A and B), H3′, H5′, H4′ (B), H5 (A), d, centred at 7.24), 7.16 (1H, t further split, J = 7.1 Hz, H6 (A)), 7.04–6.95 (4H, m, H8 (A and B), H3′, H5′ (A)), 6.93–6.86 (4H, m, H5″ (A and B), H5(B), H7 (A)), 6.76 (2H, m, H3″ (A and B)), 6.56 (1H, ddd, J = 9.0, 8.5, 2.5 Hz, H7 (B)), 2.97 (1H, d, J = 7.2 Hz, H4a (A)), 2.93 (1H, d, J = 7.2 Hz, H4a (B)), 2.81 (2H, m, CH(C6″) (A and B)), 2.67 (2H, m, CH(C6″) (A and B)), 2.61–2.41 (6H, CH_2(C2″), H9a (A and B)), 2.31, 2.29 (2H, 2d, J = 3.5 Hz, H4 (A and B)), 1.95 (2H, m, H1 (A and B)), 1.68 (4H, m, CH_3C$H_2$$CH_2$(C6″) (A and B)), 1.53 (2H, m, H3 *exo* (A and B)), 1.35–1.19 (8H, m, H3 *endo*, H2 *exo*, H10 *syn*, CH_3C*H*CH_2(C2″) (A and B)), 0.99–0.91 (8H, m, C$H_3$$CH_2$$CH_2$(C6″), H10 *anti* (A and B)), 0.83–0.69 (10H, m, C$H_3$$CH_2$$CH_2$(C2″), CH_3C*H*CH_2(C2″), H2 *endo* (A and B)).



4.3. General procedure for the synthesis of compounds ***13***

4.3.1. Reaction of o,o′-disubstituted aryl iodides, diphenylacetylene and norbornene

A DMF solution (7 ml) containing the aryl iodide (0.60 mmol), diphenylacetylene (0.72 mmol) and norbornene (0.72 mmol) was introduced under nitrogen into a Schlenk-type flask containing $Pd(OAc)_2$ (0.06 mmol) and K_2CO_3 (1.2 mmol) and the resulting mixture was stirred at 105 °C for 24 h. After cooling to room temperature the mixture was diluted with dichloromethane (ca. 15 ml) and extracted with water (3×10 ml). The organic layer was dried over Na_2SO_4; the solvent was rotary-evaporated and the products were isolated by flash column chromatography using hexane as eluent.



*4.3.2. E-9{1-(2″,6″-Dimethylphenyl)-1-phenylmethylene}-1,2,3,4,4a,9a-hexahydro-1,4-methano-1H-fluorene (**13a**: R = Me; R′ = H)*

Yield: 87%; m.p. (MeOH) 112–113 °C; ^{1}H NMR: δ 7.38 (2H, v br signal, H2′, H6′), 7.36–7.24 (4H, m, H3′, H4′, H5′, H5), 7.20–7.14 (2H, m, H6, H5″), 7.13 (1H, t, J = 7.5 Hz, H4″), 7.03 (1H, br dd, H3″), 6.96 (1H, d, J = 7.4 Hz, H8), 6.88 (1H, td, J = 7.4, 1.1 Hz, H7), 3.04 (1H, d, J = 7.3 Hz, H4a), 2.61 (1H, d, J = 7.3 Hz, H9a), 2.49 (3H, s, CH_3(C6″)), 2.35 (1H, m, H4), 2.25 (3H, s, CH_3(C2″)), 2.05 (1H, m, H1), 1.61–1.51 (1H, m, H3 *exo*), 1.40–1.26 (3H, m, H3 *endo*, H2 *exo*, H10 *syn*), 0.99 (1H, d quint., J = 9.9, 1.4 Hz, H10 *anti*), 0.93–0.82 (1H, m, H2 *endo*); ^{13}C NMR: δ 150.73 (q), 144.36 (q), 142.85 (q), 141.90 (q), 141.16 (q), 136.74 (q), 134.49 (q), 134.40 (q), 129.63 (br s, C2′, C6′), 128.17 (C3′, C5′), 127.95, 127.94, 127.93 (C3″, C5″, C6″), 126.88 (C4′), 126.73 (C4″), 125.69 (C7), 125.04 (C5), 123.97 (C8), 53.02 (C9a), 51.82 (C4a), 43.03 (C4), 40.77 (C1), 32.37 (C10), 28.93 (C3), 28.60 (C2), 21.43 (CH_3(C2″)), 20.45 (CH_3(C6″)); MS: M^+ 376 (100), *m/z* 309 (30), 229 (38), 217 (54), 203 (75), 193 (39), 167 (30), 91(25), 67(18).

*4.3.3. E-9{1-(2″,6″-Diethylphenyl)-1-phenylmethylene}-1,2,3,4,4a,9a-hexahydro-1,4-methano-1H-fluorene (**13b**: R = Et; R′ = H)*

Yield: 90%; m.p. (MeOH–CH_2Cl_2, ca. 7:3) 105–106 °C; ^{1}H NMR: δ 7.37 (2H, br d, H2′, H6′), 7.32–7.19 (6H, m, H3′, H4′, H5′, H4″, H5″, H5), 7.16 (1H, td, J = 7.2, 1.2 Hz, H6), 7.11–7.04 (2H, m, H3″, H8), 6.88 (1H, t further split, H7), 2.98 (1H, d partly overlapping with ArCH at 2.95, J = 7.3 Hz, H4a), 2.95 (1H, sext., J = 15.2, 7.6 Hz, ArCH), 2.79 (1H, sext., J = 15.2, 7.6 Hz, ArCH), 2.65 (2H, quart., J = 7.5 Hz, $ArCH_2$), 2.55 (1H, d, J = 7.3 Hz, H9a), 2.32 (1H, d, J = 4.2 Hz, H4), 1.99 (1H, d, J = 4.1 Hz, H1), 1.54 (1H, m, H3 *exo*), 1.36–1.20 (6H, m, H2 *exo*, H3 *endo*, H10 *syn*, CH_3(C2″)), 0.95 (1H, brd, J = 9,8 Hz, H10 *anti*), 0.78 (1H, m partly overlapping with CH_3 at 0.75, H2 *endo*), 0.75 (3H, t, J = 7.5 Hz, CH_3); ^{13}C NMR: δ 150.83 (q), 144.84 (q),142.33 (q), 142.00 (q), 141.85 (q), 141.72 (q), 140.11 (q), 134.34 (q), 129.86 (C2′, C6′), 128.24 (C3′, C5′), 127.97 (C6), 127.16 (C4″), 126.87 (C4′), 125.87 (C3″), 125.67 (C7), 125.41 (C5″), 125.10 (C5), 123.90 (C8), 53.10 (C9a), 51.73 (C4a), 42.97 (C4), 40.86 (C1), 32.32 (C10), 28.94 (C3), 28.58 (C2), 27.12 (CH_2), 25.40 (CH_2), 14.98 (CH_3), 14.50 (CH_3); MS: M^+404 (78), *m/z* 291 (20), 243 (17), 238 (39), 221 (100), 216 (56), 202 (50), 179 (28), 178 (28), 117 (29), 91 (47), 67 (22).

*4.3.4. E-9{1-(2″,6″-Di-i-propylphenyl)-1-phenylmethylene}-1,2,3,4,4a,9a-hexahydro-1,4-methano-1H-fluorene (**13c**: R = i-Pr; R′ = H)*

Yield: 92%; m.p. (MeOH) 134–135 °C; ^{1}H NMR: δ 7.38 (2H, br d, H2′, H6′), 7.31–7.22 (6H, m, H3′, H4′, H5, H5′, H4″, H5″), 7.17 (1H, td, J = 7.2, 1.2 Hz, H6), 7.13–7.07 (2H, m, H3″, H8), 6.88 (1H, t further split, H7), 3.44 (1H, hept., J = 6.8 Hz, ArCH), 3.21 (1H, hept., J = 6.7 Hz, ArCH), 2.98 (1H, d, J = 7.3 Hz, H4a), 2.75 (1H, d, J = 7.3 Hz, H9a), 2.36 (1H, d, J = 3.8 Hz, H4), 2.15 (1H, d, J = 3.3 Hz, H1), 1.55 (1H, m, H3 *exo*), 1.40–1.22 (12H, m, H3 *endo*, H2 *exo*, H10 *syn*, $3CH_3$ at 1.32 (d, J = 6.7 Hz), 1.31 (d, J = 6.7 Hz), 1.27 (d, J = 6.8 Hz)), 0.98 (1H, d further split, J = 9.9 Hz, H10 *anti*), 0.88 (1H, m, H2 *endo*), 0.34 (3H, d, J = 6.7 Hz, CH_3); ^{13}C NMR: δ 150.86, 147.16, 145.63, 145.51, 142.55, 142.14, 139.97, 134.19, 130.26, 128.17, 127.95, 127.72, 126.86, 125.62, 125.16, 124.02, 123.87, 123.43, 52.90 (C9a), 51.62 (C4a), 43.01 (C4), 41.04 (C1), 32.20 (C10), 31.21 (ArCH), 29.61 (ArCH), 29.05 (C3), 28.49 (C2), 26.40 (CH_3), 24.99 (CH_3), 24.84 (CH_3), 22.98 (CH_3); MS: M^+ 432 (100), *m/z* 323 (13), 291 (20), 279 (25), 245 (19), 229 (35), 203 (38), 165 (18), 129 (30), 105 (37), 91 (50), 67 (31).

*4.3.5. E-9{1-(2″,4″,6″-Trimethylphenyl)-1-phenylmethylene}-1,2,3,4,4a,9a-hexahydro-1,4-methano-1H-fluorene (**13d**: R, R′ = Me)*

Yield: 91%; m.p. (MeOH) 118–119 °C; ^{1}H NMR: δ 7.35 (2H, v br signal, H2′, H6′), 7.32–7.21 (4H, m, H3′, H4′, H5′, H5), 7.13 (1H, ddd, J = 7.5, 6.5, 1.8 Hz, H6), 6.95 (1H, br s, H3″), 6.87 (2H, m, H7, H8), 6.82 (1H, br s, H5″), 3.00 (1H, d, J = 7.3 Hz, H4a), 2.59 (1H, d, J = 7.3 Hz, H9a), 2.41 (3H, s, CH_3(C6″ downward)),

2.32 (1H, m, H4), 2.30 (3H, s, CH_3(C4″)), 2.18 (3H, s, CH_3(C2″ upward)), 2.04 (1H, m, H1), 1.61–1.49 (1H, m, H3 *exo*), 1.38–1.26 (3H, m, H3 *endo*, H2 *exo*, H10 *syn*), 0.96 (1H, d quint., J = 9.9, 1.4 Hz, H10 *anti*), 0.88 (1H, m, H2 *endo*); ^{13}C NMR: δ 150.77 (q), 144.54(q), 142.10 (q), 141.60 (q), 140.11 (q), 136.56 (q), 136.07 (q), 134.59 (q), 134.32 (q), 129.69 (br s, C2′, C6′), 128.86 (C5″), 128.79 (C3″), 128.26 (C3′, C5′), 127.94 (C6), 126.87 (C4′), 125.76 (C7), 125.11 (C5), 124.05 (C8), 53.11 (C9a), 51.89 (C4a), 43.20 (C4), 40.90 (C1), 32.47 (C10), 29.06 (C3), 28.75 (C2), 21.42 (CH_3(C2″)), 21.14 (CH_3(C4″)), 20.44 (CH_3(6″)); MS: M^+ 390 (100), *m*/*z* 323 (23), 229 (45), 203 (80), 174 (30), 145 (22), 91 (25).

The reaction was also carried out by adding Bu_4NBr (6.0 mmol), using: 2,4,6-trimethyliodobenzene (0.60 mmol), diphenylacetylene (0.72 mmol), norbornene (0.72 mmol), $Pd(OAc)_2$ (0.06 mmol) and K_2CO_3 (1.2 mmol) in DMF (7 ml). The reaction led to a 93% yield with a 97% conversion of the aryl iodide. Using $KHCO_3$ (2.4 mmol) in place of K_2CO_3 led to 71% yield of **13d**, conversion of the aryl iodide being 86%.

*4.3.6. Reaction of 2,4,6-trimethyliodobenzene, diphenylacetylene and bicyclo[2.2.2]octene: synthesis of E-9 {1-(2,4,6-trimethylphenyl)-1-phenylmethylene}-1,2,3,4,4a,9a-hexahydro-1,4-ethano-1H-fluorene (**16**)*

The reaction was carried out following the general procedure reported for the synthesis of compounds **13** using bicyclo[2.2.2]octene in place of norbornene.

Yield: 89%; m.p. (MeOH) 101–102 °C; ^{1}H NMR: δ 7.35 (2H, v br signal, H2′, H6′), 7.32–7.21 (3H, m, H3′, H4′, H5′), 7.21–7.08 (2H, m, H5, H6), 6.97–6.85 (3H, m, H8, H5″, H7), 6.76 (1H, br s, H3″), 3.27 (1H, dd, J = 9.7, 3.8 Hz, H4a), 2.78 (1H, ddd, J = 9.7, 3.0, 1.0 Hz, H9a), 2.38 (3H, s, CH_3(C6″)), 2.26 (3H, s, CH_3(C4″)), 2.11 (3H, s, CH_3(C2″)), 1.94 (1H, m, H4), 1.75–1.52 (3H, m, H2 *exo*, H3 *exo*, H3 *endo*), 1.41 (1H, m, H1), 1.32–1.18 (5H, m, H2 *endo*, 2H10, 2H11); ^{13}C NMR: δ 151.06 (q), 144.88(q), 141.73 (q), 141.19 (q), 139.77 (q), 136.86 (q), 135.95 (q), 134.80 (q), 134.25 (q), 129.72 (br s, C2′, C6′), 128.68 (C5″), 128.58 (C3″), 128.19 (C3′, C5′), 127.63 (C6), 126.78 (C4′), 125.76 (C7), 124.89 (C5), 124.12 (C8), 46.76 (C9a), 45.83 (C4a), 28.89 (C4), 27.87 (C1), 26.26 (C3), 25.81 (C2), 21.46 (C10*), 21.26 (C11*), 21.01 (CH_3(C4″)), 20.90 (CH_3(C2″)), 20.39 (CH_3(C6″)); MS: M^+ 404 (100), *m*/*z* 389 (16), 313 (15), 229 (20), 91 (18).

*4.3.7. Reaction of 2-n-propyliodobenzene, n-propyl chloride, diphenylacetylene and norbornene: synthesis of E-9 {1-(2,6-di-n-propylphenyl)-1-phenylmethylene}-1,2,3,4,4a,9a-hexahydro-1,4-methano-1H-fluorene (**13e**: R = n-Pr; R′ = H)*

The reaction was carried out following the general procedure reported above for the synthesis of compounds **13** using 2-*n*-propyliodobenzene as the aryl iodide and adding *n*-propyl chloride (2.4 mmol).

Yield: 70%. ^{1}H NMR (400.13 MHz): δ 7.35 (2H, v br signal, H2′, H6′), 7.30–7.17 (6H, m, H3′, H5′, H4′, H5, H4″, H5″), 7.13 (1H, td, J = 7.1, 1.1 Hz, H6), 7.09–7.01 (2H, m, H8, H3″), 6.95 (1H, t further split, H7), 2.96 (1H, br d, J = 7.2 Hz, H4a), 2.86 (1H, m, ArCH(C6″)), 2.69 (1H, m, ArCH(C6″)), 2.62 (1H, m, ArCH(C2″)), 2.54 (1H, br d, J = 7.2 Hz, H9a), 2.48 (1H, m, ArCH (C2″)), 2.29 (1H, m, H4), 1.97 (1H, m, H1), 1.72 (2H, m, CH_3CH_2(C6″)), 1.51 (1H, m, H3 *exo*), 1.33–1.20 (4H, m, H3 *endo*, H2 *exo*, H10 *syn*, CH_3CH (C2″)), 0.95 (3H, t, J = 7.3 Hz, CH_3(C6″)), 0.92 (1H, d quintets partly overlapping with CH_3, H10 *anti*), 0.79–0.71 (5H, m, CH_3CH(C2″), CH_3(C2″), H2 *endo*); ^{13}C NMR (100.6 MHz): δ 150.84 (q), 144.80 (q), 142.09 (q), 142.04 (q), 141.97 (q), 141.31 (q), 138.93 (q), 134.35 (q), 129.83 (br signal, C2′, C6′), 128.17 (C3′, C5′), 127.90 (C6), 126.87 (C4′, C4″), 126.46 (C3″), 125.94 (C5″), 125.63 (C7), 125.07 (C5), 124.03 (C8), 53.13 (C9a), 51.79 (C4a), 42.97 (C4), 40.84 (C1), 36.63 ($ArCH_2$(C2″)), 34.80 ($ArCH_2$(C6″)), 32.37 (C10), 28.94 (C3), 28.60 (C2), 28.81 (CH_2CH_3), 28.78 (CH_2CH_3), 14.60 (CH_3 (C6″)), 14.33 (CH_3(C2″)); MS: M^+ 432 (75), *m*/*z* 291(22), 249 (33), 215 (67), 179 (98), 131 (39), 91 (100), 67 (40).

*4.3.8. E-9 {1-(2,6-Di-n-butylphenyl)-1-phenylmethylene}-1,2,3,4,4a,9a-hexahydro-1,4-methano-1H-fluorene (**13f**: R = n-Bu; R′ = H)*

The reaction was carried out following the procedure reported above, using 2-*n*-butyliodobenzene and *n*-butyl chloride in place of 2-*n*-propyliodobenzene and *n*-propyl chloride, respectively.

Yield: 94%. ^{1}H NMR: δ 7.36 (2H, br d, H2′, H6″), 7.28 (2H, m, H3′, H5′), 7.24–7.19 (4H, m, H4′, H5, H4″, H5″), 7.15 (1H, td, J = 7.2 Hz, 1.1 Hz, H6), 7.12–7.01 (2H, m, H8, H3″), 6.87 (1H, t further split, H7), 2.97 (1H, d, J = 7.3 Hz, H4a), 2.89 (1H, m, ArCH), 2.73 (1H, m, ArCH), 2.64–2.46 (3H, m, $ArCH_2$, H9a), 2.32 (1H, d, J = 4.1 Hz, H4), 1.99 (1H, d, J = 4.2 Hz, H1), 1.69 (2H, m, $ArCH_2CH_2$), 1.53 (1H, m, H3 *exo*), 1.44–0.65 (17H, m); MS: M^+ 460 (41), *m*/*z* 302 (8), 291 (14), 239 (37), 215 (32), 203 (28), 179 (35), 145 (22), 91 (100), 67 (31), 57 (23).

Using *n*-butyl bromide in place of the corresponding chloride compound **13f** was isolated in 37% yield together with a 39% of unconverted aryl iodide.

4.4. X-ray diffraction measurements

Crystals of compound **13a** (R = Me, R′ = H) suitable for X-ray determination were obtained by slow crystallisation from methanol. The X-ray data were collected at room temperature on a Siemens AED diffractometer [23] using a colourless prismatic specimen of

0.13x0.21x0.29 mm. The compound, $C_{29}H_{28}$, was monoclinic, space group $P2_1/n$ with cell parameters $a = 9.139(2)$ Å, $b = 15.708(3)$ Å, $c = 14.918(2)$ Å, $\beta = 94.14(4)°$. Using the Cu Kα radiation, $\lambda = 1.5418$ Å, a total of 4026 independent reflections were measured in the 3–70° θ range and 1861 of them were considered observed at 2σ level. The structure was solved by direct methods with SIR97 [24] and refined using F^2 with SHELX97 [25]. All the H atoms, found in a ΔF map, were refined isotropically. A total of 375 parameters were refined and the the final R value was 0.069, $R_w = 0.221$ with $w = 1/(\sigma^2 F_o^2 + 0.0175P)^2$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC No. 234463 for compound **13a**. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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References

[1] J. Tsuji, Palladium Reagents and Catalysts: Innovation in Organic Synthesis, Wiley, Chichester, 1995.
[2] (a) M. Catellani, F. Frignani, A. Rangoni, Angew. Chem., Int. Ed. Engl. 36 (1997) 119;
(b) M. Catellani, Pure Appl. Chem. 74 (2002) 63;
(c) M. Catellani, Synlett (2003) 298.
[3] (a) M. Catellani, M.C. Fagnola, Angew. Chem., Int. Ed. Engl. 33 (1994) 2421;
(b) M. Catellani, G.P. Chiusoli, J. Organomet. Chem. 346 (1988) C27;
(c) M. Catellani, B.E. Mann, J. Organomet. Chem. 390 (1990) 251.
[4] P. Fitton, E.A. Rick, J. Organomet. Chem. 28 (1971) 287.
[5] (a) H. Horino, M. Arai, N. Inoue, Tetrahedron Lett. (1974) 647;
(b) C.-S. Li, C.-H. Cheng, F.-L. Liao, S.-L. Wang, Chem. Commun. (1991) 710;
(c) M. Portnoy, Y. Ben-David, I. Rousso, D. Milstein, Organometallics 13 (1994) 3465;
(d) M. Catellani, C. Mealli, E. Motti, P. Paoli, E. Perez-Carreno, P.S. Pregosin, J. Am. Chem. Soc. 124 (2002) 4336.
[6] (a) J. Cámpora, P. Palma, E. Carmona, Coord. Chem. Rev. 193–195 (1999) 207;
(b) M. Catellani, G.P. Chiusoli, J. Organomet. Chem. 346 (1988) C27;
(c) C.-H. Liu, C.-S. Li, C.-H. Cheng, Organometallics 13 (1994) 18;
(d) M. Catellani, G.P. Chiusoli, J. Organomet. Chem. 425 (1992) 151;
(e) G. Dyker, Chem. Ber. 130 (1997) 1567;
(f) A.D. Ryabov, Chem. Rev. 90 (1990) 403.
[7] (a) A.J. Canty, Acc. Chem. Res. 25 (1992) 83 and references therein;
(b) W. de Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 8 (1989) 2907;
(c) R. van Asselt, E. Rijnberg, C.J. Elsevier, Organometallics 13 (1994) 706.
[8] G. Bocelli, M. Catellani, S. Ghelli, J. Organomet. Chem. 458 (1993) C12.
[9] M.C. Gallazzi, L. Porri, G. Vitulli, J. Organomet. Chem. 97 (1975) 131.
[10] M. Catellani, in: E.-I. Negishi (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, vol. 2, Wiley, New York, 2002 (Chapter IV. 6.2).
[11] (a) R.F. Heck, J.P. Nolley, J. Am. Chem. Soc. 96 (1972) 2320;
(b) A. de Meijere, F.E. Meyer, Angew. Chem., Int. Ed. Engl. 106 (1994) 2473;
(c) W. Cabri, I. Candiani, Acc. Chem. Res. 28 (1995) 2;
(d) I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.
[12] (a) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457;
(b) M. Catellani, E. Motti, M. Minari, Chem. Commun. (2000) 157.
[13] (a) L. Cassar, J. Organomet. Chem. 93 (1975) 253;
(b) K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 50 (1975) 4467.
[14] (a) M. Catellani, G.P. Chiusoli, Tetrahedron Lett. 23 (1982) 4517;
(b) M. Catellani, G.P. Chiusoli, A. Mari, J. Organomet. Chem. 275 (1984) 129;
(c) C.-H. Liu, C.-S. Li, C.-H. Cheng, Organometallics 13 (1994) 18;
(d) M. Catellani, B. Marmiroli, M.C. Fagnola, D. Acquotti, J. Organomet. Chem. 507 (1996) 157.
[15] U. Bersellini, M. Catellani, G.P. Chiusoli, W. Giroldini, G. Salerno, in: M. Tsutsui (Ed.), Fundamental Research in Homogeneous Catalysis, vol.3, Plenum Press, New York, 1979, p. 893.
[16] G. Dyker, A. Kellner, Tetrahedron Lett. 35 (1994) 7633.
[17] C. Zhou, D.E. Emrich, R.C. Larock, Org. Lett. 5 (2003) 1579.
[18] D. Brown, R. Grigg, V. Sridharan, V. Tambyrajah, M. Thornton-Pett, Tetrahedron 54 (1998) 2595.
[19] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[20] M.S. Lesslie, J.M. Mayer, J. Chem. Soc. 614 (1961).
[21] A.L. Casalnuovo, J.C. Calabrese, J. Am. Chem. Soc. 112 (1990) 4324.
[22] G.W. Kabalka, L. Wang, R.M. Pagni, Tetrahedron 57 (2001) 8017.
[23] D. Belletti, A. Cantoni, G. Pasquinelli. Gestione on Line di Diffrattometro a Cristallo Singolo Siemens AED con Personal Computer. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy, 1993, Internal Report 1-93.
[24] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, Acta Crystallogr. 32 (1999) 115.
[25] G.M. Sheldrick, SHELX-97: Program for Crystal Structure Refinement, University of Göttingen, Germany.